# Effect of Wastewater Sample Pre-Treatment on Determination of Selected Heavy Metals Using ICP-MS Method

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*Abstract*

*Polychlorinated substances, polyaromatic hydrocarbons, heavy metals and pesticides are among the priority even at low concentrations. The problem, however, is that such low concentrations are impossible to measure using most available methods. This research focused on the determination of selected priority substances – heavy metals, namely lead and cadmium, in which the determination of Pb and Cd in wastewater by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was preceded by water sample pre-treatment. The paper deals with the influence of the pre-treatment on the resulting measured values. Two processes were selected as pre-treatment processes. The first pre-treatment procedure was a simple filtration using a filter paper for moderate filtration. As the second procedure, we applied decomposition of the sample by nitric acid in the open system. The pre-treated wastewater samples were subsequently examined using ICP-MS. Based on the obtained results, we can conclude that decomposition of the sample by nitric acid in the open system is a more suitable pre-treatment method for water samples.*

**Keywords:** *heavy metals, lead, cadmium, wastewater, pre-treatment filtration*

## Introduction

Priority substances are defined by the Water Framework Directive as a significant risk to the aquatic environment. Priority substances are persistent, toxic and have a high accumulation capacity. They also include heavy metals - lead and cadmium, which this research is focused on. [1,2]

Lead is obtained from lead ore – Galenite (PbS). Especially in the past, there were significant anthropogenic sources, when lead made parts of gasoline, resulting in lead accumulation in the vegetation along the roads. Lead contamination also occurred when water was in contact with corrosive parts of water piping. At present, lead is contained in wastewaters from ore processing and battery production. [3,4,5]

Cadmium is potentially carcinogenic and teratogenic, so its use is minimal. It gets into the aquatic environment from the industry (electroplating and battery production) and fertilizers. It is mainly accumulated in water sediments. In humans, cadmium accumulates mainly in kidneys and liver. Cadmium causes decalcification of bones and affects blood pressure. [3,4,6]

In the Czech Republic, heavy metal concentrations in wastewater are regulated by Regulation 401/2015 Coll., which also contains environmental quality standards (EQS). The standards specify the EQS-AA limits: an environmental quality standard expressed as an annual average value and EQS-MAC: an environmental quality standard expressed as the maximum allowable concentration that must not be exceeded. For the purposes of this paper, the EQS-MAC limits have been used to assess and compare the measured values. The permissible values of Cd and Pb concentration according to NEK-MAC are given in Table 1. According to the measured values of Cd concentration, wastewater is divided into five classes.

Priority substances have a negative impact on the aquatic environment even at very low concentrations. Such low concentrations are generally difficult to determine. For this reason, ICP-MS method was chosen for this research. This method is able to detect concentrations in ppb units.

Sample pre-processing is very important for ICP-MS. The aim of the pre-treatment is to ensure the removal of interfering compounds and to concentrate the measured analyte in the sample. Basic processes of pre-treatment include, for example, filtration, centrifugation, extraction or microwave decomposition of the sample. [8]

## Materials and Methods

Two sewage samples were selected for this experiment. The first was wastewater taken from the municipal Waste-

Tab. 1. Allowable concentrations of cadmium and lead for each class according to EQS-MAC [7]
Tab. 1. Dopuszczalne stężenia kadmu i ołowiu dla każdej klasy zgodnie z EQS-MAC [7]

| Heavy metal | Class | EQS-MAC [ppb] |
|---|---|---|
| Cd | 1 | ≤ 0.45 |
| | 2 | 0.45 |
| | 3 | 0.6 |
| | 4 | 0.9 |
| | 5 | 1.5 |
| Pb | | 14 |

Tab. 2. Results obtained by ICP-MS analysis for Sample 1
Tab. 2. Wyniki uzyskane za pomocą analizy ICP-MS dla próbki 1

| | Filtration | | Decomposition | |
|---|---|---|---|---|
| | Cd [ppb] | Pb [ppb] | Cd [ppb] | Pb [ppb] |
| 1 | 0.0593 | 0.1089 | 0.0834 | 0.9691 |
| 2 | 0.0553 | 0.1311 | 0.0851 | 1.0449 |
| 3 | 0.0566 | 0.1188 | 0.0723 | 1.0270 |
| **avg.** | **0.0571** | **0.1196** | **0.0803** | **1.0137** |

Tab. 3. Results obtained by ICP-MS analysis for Sample 2
Tab. 3. Wyniki uzyskane za pomocą analizy ICP-MS dla próbki 2

| | Filtration | | Decomposition | |
|---|---|---|---|---|
| | Cd [ppb] | Pb [ppb] | Cd [ppb] | Pb [ppb] |
| 1 | 0.5220 | 0.3679 | 1.2504 | 2.7350 |
| 2 | 0.5652 | 0.3163 | 1.3236 | 2.7495 |
| 3 | 0.5378 | 0.3395 | 1.2504 | 2.6925 |
| **avg.** | **0.5417** | **0.3412** | **1.2748** | **2.7257** |

water Treatment Plant (Sample 1). The second sample can be referred to as industrial wastewater, because it comes from a wastewater treatment plant of the company that deals with the production of nickel-cadmium batteries (Sample 2).

Selected samples were analyzed by ICP-MS. This method is one of the modern analytical methods using which the trace amount of individual elements contained in the analyzed samples can be determined. One of the advantages of this method is the possibility of fast and multi-element analysis. The basis of ICP-MS is the ion source, which serves to ionize the elements in the sample. The resulting ions are further fed to a mass analyzer. In the analyzer, the individual ions are divided by their mass and charge (m/z). This is followed by their detection, where the ions separated by the analyzer pass into the detector, whose main task is to convert the ion current into an electron current. This is followed by a PC evaluation. [9, 10, 11]

Before using the ICP-MS analytical method, it is important to pre-treat all the analyzed samples.

In this research, both samples were pre-treated using two procedures. The first procedure was simple filtration. Filtration paper was used for medium filtration rate. 50 ml of each sample were filtered. After filtration, 0.5 ml of nitric acid was added to each sample for stabilization. All chemicals used in this analysis must be of p.p purity.

As the second procedure we chose the decomposition of the sample by nitric nitrate in the open system. 50 ml of each sample was boiled. The boil was terminated when the volume of boiled samples dropped to half – 25 ml sample. After boiling, the samples were cooled and also filtered through medium filtering paper. The filtrates obtained were filled up to 50 ml with distilled water.

All the pre-treated samples were further analyzed by ICP-MS the next day. Analysis of each sample was performed 3 times, to avoid measurement errors. Analyses were performed on the instrument Analytik Jena PlasmaQuant MS Elite.

**Result and Discussion**

The results obtained by ICP-MS analysis are summarized in Tables 2 and 3. The values of each individual measurement were averaged and further compared with the EQS-MAC.

The results show that the concentration of cadmium in Sample 1 after both pre-treatment methods is very low and the results are of the order of magnitude, with all the measured values of the sample

pre-treated with nitric acid decomposition are higher. By comparison with EQS-MAC this sample belongs to class 1 in indicator Cd.

After analysis of sample 2, which was pre-treated by filtration, concentration of cadmium of 0.5417 ppb was measured. In this case, sample belongs to class 2 according to EQS-MAC. After nitric acid decomposition, the sample had a Cd concentration of 1.2748 ppb, which corresponds to class 4 according to EQS-MAC. The Cd concentration values obtained differ. After both pre-treatment methods, Pb concentrations measured for Sample 2 were lower than the EQS-MAC value. These values also differ from one another. Again, the values found for samples that were pre-treated with simple filtration are lower.

The heavy metals concentration values measured in the municipal waste water (Sample 1) were lower than the concentrations found in industrial wastewater (Sample 2).

**Conclusion**

The results show that the pre-treatment of the sample affects the subsequent determination of selected heavy metals in wastewater samples. The concentration of both metals was shown to be lower for samples that were only filtered prior to ICP-MS analysis. Thus, according to EQS-MAC these samples belong to a lower quality class and appear to be of superior quality. However, for ICP-MS analysis, it is preferable to pre-treat the analyzed samples by decomposing the sample with nitric acid in an open system. By this pre-treatment process, sufficient removal of interfering compounds in the sample was achieved over simple filtration.

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## *Wpływ wstępnej obróbki próbek ścieków na oznaczanie wybranych metali ciężkich metodą ICP-MS*

*Zawartość substancje polichlorowanych, węglowodorów poliaromatycznych, metali ciężkich i pestycydów ma ogromne znaczenie nawet przy niskich stężeniach. Problem polega na tym, że niskich stężeń nie można zmierzyć przy użyciu większości dostępnych metod. Badania koncentrowały się na oznaczeniu wybranych substancji priorytetowych – metali ciężkich, a mianowicie ołowiu i kadmu, w których oznaczanie Pb i Cd w ściekach metodą indukcyjnie sprzężonej plazmowej spektrometrii masowej (ICP-MS) poprzedziło wstępne uzdatnianie próbki wody. Artykuł dotyczy wpływu obróbki wstępnej na uzyskane wartości pomiarowe. Dwa procesy wybrano jako procesy obróbki wstępnej. Pierwszą procedurą wstępnej obróbki była prosta filtracja z użyciem bibuły filtracyjnej do umiarkowanej filtracji. W drugiej procedurze zastosowano rozkład próbki kwasem azotowym w układzie otwartym. Wstępnie oczyszczone próbki ścieków zostały następnie zbadane przy użyciu ICP-MS. Na podstawie uzyskanych wyników stwierdzono, że rozkład próbki kwasem azotowym w układzie otwartym jest bardziej odpowiednią metodą wstępnej obróbki próbek wody.*

***Słowa kluczowe:*** *metale ciężkie, ołów, kadm, ścieki, filtracja wstępna*